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Dissipative Van der Waals interaction between a small particle and a metal surface

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Abstract

We use a general theory of the fluctuating electromagnetic field to calculate the friction force acting on a small neutral particle, e.g., a physisorbed molecule, or a nanoscale object with arbitrary dispersive and absorptive dielectric properties, moving near a metal surface. We consider the dependence of the electromagnetic friction on the temperature T , the separation d , and discuss the role of screening, non-local and retardation effects. We find that for high resistivity materials, the dissipative van der Waals interaction can be an important mechanism of vibrational energy relaxation of physisorbed molecules, and friction for microscopic solids. Several controversial topics related to electromagnetic dissipative shear stress is considered. The problem of local heating of the surface by an STM tip is also briefly commented on.

I. Introduction

There are an increasing number of investigations of the dissipative van der Waals interaction, and the heat transfer between nanostructures, due to the evanescent fluctuating electromagnetic field^{1,2,3,4,5,6,7,8,9,10,11} in connection with scanning probe microscopy,^{12,13,14} the quartz-crystal microbalance,^{15,16} the surface force apparatus technique,¹⁷ the frictional drag experiments between 2D electron system¹⁸ and the scanning thermal microscopy under ultrahigh vacuum conditions.¹⁹

The general theory of the fluctuating electromagnetic field was developed by Rytov²⁰ and applied for studying the conservative and dissipative part of the van der Waals interaction,^{4,5,6,21} the heat transfer between macroscopic bodies and nanostructures^{9,22,23,24} and the frictional drag force between 2D-electron systems.¹⁰ Despite numerous contributions to the literature, the field of the dissipative van der Waals interaction is very controversial, and some fundamental problems remain unsolved. In particular, the authors of Ref.^{5,6} (and reference therein) argue that the linear (in the sliding velocity) friction force between bodies, due to dissipative van der Waals interaction, is non-vanishing at zero temperature, in sharp contrast to the results of other authors.^{1,2,4,9} In Appendix A we show that the basic equation in^{5,6} is incorrect, and that a correct treatment gives a vanishing linear friction at $T = 0 K$. The friction force acting on a particle moving near a wall originating from the fluctuating electromagnetic field was considered recently in.¹¹ The friction force was calculated from the electromagnetic energy losses in the metal substrate, arising from the dipole field induced by the fluctuating electromagnetic field from the metal. However, as it is shown in Appendix A, such an approach is incorrect because the friction force is determined by strong compensation between several processes involving loss and gain of electromagnetic energy, which were not considered in.¹¹ We note also that the energy losses in the metal substrate, due to the dipole field induced by the metal field, are much smaller than the energy losses of the metal field in the particle. There are also processes of energy losses of the dipole field in the metal substrate due to spontaneous fluctuation of dipole moment which were also not considered in.¹¹

Another common belief is that it is necessary to go beyond second order perturbation theory when calculating the friction force acting on a physisorbed molecules at temperatures $k_B T \ll \Delta$, where Δ is the energy of

the first excited state of the molecule relative to the ground state.^{1,25} This conclusion follows from the formula^{1,9}

$$F_{fric} = \frac{3\hbar V}{2\pi d^5} \int_0^\infty d\omega \left(-\frac{\partial n(\omega)}{\partial \omega} \right) \text{Im} \left(\frac{\varepsilon(\omega) - 1}{\varepsilon(\omega) + 1} \right) \text{Im}\alpha(\omega), \quad (1)$$

where

$$n(\omega) = \frac{1}{e^{\hbar\omega/k_B T} - 1} \quad (2)$$

is the Bose-Einstein factor, $\varepsilon(\omega)$ is a metal dielectric constant and $\alpha(\omega)$ is the dipole polarizability. Since for physisorbed molecules, $\text{Im}\alpha(\omega) \sim \delta(\omega - \Delta/\hbar)$, the friction force approach zero exponentially as $T \rightarrow 0$. Thus, $F \propto \exp(-\Delta/k_B T)$. This situation is similar to that of the “vacuum” friction between two flat surfaces,^{2,4} where the frictional stress involves a product of the imaginary part of the reflection factors for both surfaces. As a result, “vacuum” friction is non-vanishing only between two metal surfaces: it vanish for metal-dielectric or dielectric-dielectric systems. Formula (1) does not include screening effects which become important for sufficiently small separations between the molecule and the metal surface.

In the present paper we use the theory of the fluctuating electromagnetic field to calculate directly the friction force acting on a fluctuating point dipole for arbitrary direction of motion, and taking into account screening, retardation and non-local optic effects. A striking result we find is that, for small separations, the screening effects become crucial, and in fact dominate the friction force between the fluctuating point dipole and the metal surface, because they give a contribution to the friction force which is proportional to the absolute value of the molecule polarizability instead of it imaginary part.

There is fundamental difference between “vacuum” friction for two flat surfaces and for point dipole above a flat surface. In the former case, scattering of electromagnetic waves by the surfaces conserves the parallel momentum. Hence, the only possible process of momentum transfer between two flat surfaces is the emission of electromagnetic waves by one body, and subsequent absorption by another body. For the evanescent waves this process gives a contribution which is proportional to product of the imaginary part of the reflection factors for both surfaces. In the case of a particle above flat surface, the component of the momentum parallel to the surface can change during scattering by the particle, resulting in momentum transfer. This

process gives a contribution which is proportional to product of imaginary part of reflection factor for metal at different value of momentum parallel to surface and absolute value of the point dipole polarizability. The results obtained are applied to the problem of the vibrational energy relaxation of the physisorbed molecule, and the friction and the heat transfer between an STM tip and the metal surface.

II. Calculation of the fluctuating electromagnetic field

Following Lifshitz,²¹ to calculate the fluctuating electromagnetic field we use the general theory of Rytov (see Ref.^{20,24}). This method is based on the introduction of a fluctuating current or polarization density in Maxwell equations (analogous to, for example, the introduction a “random” force in the theory of Brownian motion of a particle). We consider a semi-infinite metal having flat surface which coincides with xy - coordinate plane, and with the z - axes pointed along the upward normal. A point dipole located at $\mathbf{r}_0 = (0, 0, d)$, performing small amplitude vibrations with the displacement vector $\mathbf{u}(t) = \mathbf{u}_0 e^{-i\omega_0 t}$. To linear order in the vibrational coordinate $\mathbf{u}(t)$, the polarization density corresponding to the point dipole can be written in the form:

$$\mathbf{p}(\mathbf{r}, t) = \mathbf{p}_0 \delta(\mathbf{r} - \mathbf{r}_0) e^{-i\omega t} + \mathbf{p}_1(\mathbf{r}, \omega) e^{-i(\omega + \omega_0)t}, \quad (3)$$

$$\mathbf{p}_1(\mathbf{r}, \omega) = \mathbf{p}_1 \delta(\mathbf{r} - \mathbf{r}_0) - \mathbf{p}_0 \mathbf{u}_0 \cdot \frac{\partial}{\partial \mathbf{r}} \delta(\mathbf{r} - \mathbf{r}_0), \quad (4)$$

where $\mathbf{p}_0 = \mathbf{p}^f + \alpha(\omega) \mathbf{E}_0$, $\mathbf{p}_1 = \alpha(\omega + \omega_0) \mathbf{E}_1$, $\mathbf{E}(t) = \mathbf{E}_0 e^{-i\omega t} + \mathbf{E}_1 e^{-i(\omega + \omega_0)t}$ is an external electric field at the position of the dipole, $\alpha(\omega)$ is the dipole polarizability, \mathbf{p}^f is a fluctuating dipole moment with spectral density function which accordingly to fluctuation-dissipation theorem²⁶ is given by:

$$\langle p_i^f p_j^{f*} \rangle_\omega = 4\pi A(\omega, T) \text{Im} \alpha(\omega) \delta_{ij} \quad (5)$$

$$A(\omega, T) = \frac{\hbar}{(2\pi)^2} \left(\frac{1}{2} + n(\omega) \right), \quad (6)$$

Outside the metal the electric field is given by the sum of the electric field from the point dipole, $\mathbf{E}_d(\mathbf{r}, t)$, and the electric field from the metal induced by point dipole, $\mathbf{E}_d^{ind}(\mathbf{r}, t)$, and the electric field from the metal $\mathbf{E}^s(\mathbf{r}, t)$ in

absence of point dipole and originated from thermal and quantum fluctuation of polarization inside the metal:

$$\mathbf{E}^{total}(\mathbf{r}, t) = \mathbf{E}_d(\mathbf{r}, t) + \mathbf{E}_d^{ind}(\mathbf{r}, t) + \mathbf{E}^s(\mathbf{r}, t) \quad (7)$$

In our consideration we will need only the last two fields. The electric field $\mathbf{E}_d^{ind}(\mathbf{r}, t)$ can be written in the form:

$$\mathbf{E}_d^{ind}(\mathbf{r}, t) = \mathbf{E}_0(\mathbf{r}, \omega)e^{-i\omega t} + \mathbf{E}_1(\mathbf{r}, \omega + \omega_0)e^{-i(\omega + \omega_0)t} \quad (8)$$

$$E_{0i}(\mathbf{r}, \omega) = D_{ij}(\mathbf{r}, \mathbf{r}_0, \omega)p_{0j} \quad (9)$$

$$E_{1i}(\mathbf{r}, \omega + \omega_0) = D_{ij}(\mathbf{r}, \mathbf{r}_0, \omega + \omega_0)p_{1j} + \mathbf{u}_0 \cdot \frac{\partial}{\partial \mathbf{r}'} D_{ij}(\mathbf{r}, \mathbf{r}', \omega + \omega_0)_{\mathbf{r}'=\mathbf{r}_0} p_{0j} \quad (10)$$

where $\tilde{D}_{ik}(\mathbf{r}, \mathbf{r}', \omega) = D_{ik}^0(\mathbf{r}, \mathbf{r}', \omega) + D_{ik}(\mathbf{r}, \mathbf{r}', \omega)$ obeys the equations²⁷

$$\left[\nabla_i \nabla_k - \delta_{ik}(\nabla^2 + (\omega/c)^2)\varepsilon(\mathbf{r}) \right] \tilde{D}_{kj}(\mathbf{r}, \mathbf{r}', \omega) = (4\pi\omega^2/c^2)\delta_{ij}\delta(\mathbf{r} - \mathbf{r}') \quad (11)$$

$$\left[\nabla'_j \nabla'_k - \delta_{jk}(\nabla'^2 + (\omega/c)^2)\varepsilon(\mathbf{r}') \right] \tilde{D}_{ik}(\mathbf{r}, \mathbf{r}', \omega) = (4\pi\omega^2/c^2)\delta_{ij}\delta(\mathbf{r} - \mathbf{r}'), \quad (12)$$

the function $D_{ik}^0(\mathbf{r}, \mathbf{r}', \omega)$ obeys the inhomogeneous equations (11-12) for free space, and $D_{ik}(\mathbf{r}, \mathbf{r}', \omega)$ outside the metal determines an induced electric field and obeys the homogeneous equations (11-12). The solution of the equations (11-12) is described in detail in Appendix B. The electric field from the metal $\mathbf{E}^s(\mathbf{r}, t) = \mathbf{E}^s(\mathbf{r}, \omega)e^{-i\omega t}$ is characterized by the following spectral density function^{9,27}

$$\langle E_i^s(\mathbf{r}) E_j^{s*}(\mathbf{r}') \rangle_\omega = 4\pi A(\omega, T) \text{Im} D_{ij}(\mathbf{r}, \mathbf{r}', \omega) \quad (13)$$

The electric fields \mathbf{E}_0 and \mathbf{E}_1 at the position of point dipole can be found from the condition of self-consistency:

$$E_{0i} = D_{ii}(\mathbf{r}_0, \mathbf{r}_0, \omega)p_{0i} + E_i^s(\mathbf{r}_0, \omega), \quad (14)$$

$$E_{1i} = D_{ii}(\mathbf{r}_0, \mathbf{r}_0, \omega + \omega_0)\alpha(\omega + \omega_0)E_{1i} + \mathbf{u}_0 \cdot \frac{\partial}{\partial \mathbf{r}} \left(E_i^s(\mathbf{r}, \omega) + D_{ij}(\mathbf{r}_0, \mathbf{r}, \omega + \omega_0)p_{0j} + D_{ij}(\mathbf{r}, \mathbf{r}_0, \omega)p_{0j} \right)_{\mathbf{r}=\mathbf{r}_0}. \quad (15)$$

In (14-15) we use that $D_{ik}(\mathbf{r}, \mathbf{r}) = \delta_{ik}D_{ii}(\mathbf{r}, \mathbf{r})$. From (14-15) we get:

$$E_{0i} = \frac{E_i^s(\mathbf{r}_0) + D_{ii}(\mathbf{r}_0, \mathbf{r}_0, \omega)p_i^f}{1 - \alpha(\omega)D_{ii}(\mathbf{r}_0, \mathbf{r}_0, \omega)}, \quad (16)$$

$$p_{0i} = \frac{p_i^f + \alpha(\omega)E_i^s(\mathbf{r}_0, \omega)}{1 - \alpha(\omega)D_{ii}(\mathbf{r}_0, \mathbf{r}_0, \omega)}, \quad (17)$$

$$E_{1i} = \mathbf{u}_0 \cdot \frac{\partial}{\partial \mathbf{r}} \frac{\left(E_i^s(\mathbf{r}) + D_{ij}(\mathbf{r}_0, \mathbf{r}, \omega + \omega_0)p_{0j} + D_{ij}(\mathbf{r}, \mathbf{r}_0, \omega)p_{0j} \right)}{1 - \alpha(\omega + \omega_0)D_{ii}(\mathbf{r}_0, \mathbf{r}_0, \omega + \omega_0)} \Big|_{\mathbf{r}=\mathbf{r}_0}. \quad (18)$$

III. Force of friction on dipole

The total electromagnetic force on a fluctuating dipole is determined by the Lorentz force:

$$\mathbf{F} = \int_{-\infty}^{\infty} d\omega \int d^3r \left(\langle \rho \mathbf{E} \rangle + \frac{1}{c} \langle \mathbf{j} \times \mathbf{B} \rangle \right), \quad (19)$$

where the integration is over the volume of the dipole vibrating in the external electric field

$$\mathbf{E}(\mathbf{r}, t) = (\mathbf{E}_0(\mathbf{r}, \omega) + \mathbf{E}^s(\mathbf{r}, \omega)) e^{-i\omega t} + \mathbf{E}_1(\mathbf{r}, \omega + \omega_0) e^{-i(\omega + \omega_0)t} \quad (20)$$

and magnetic induction field which can be obtained from the electric field using Maxwell's equations

$$\mathbf{B}(\mathbf{r}, t) = -ic \nabla \times \left((\mathbf{E}_0(\mathbf{r}, \omega) + \mathbf{E}^s(\mathbf{r}, \omega)) \frac{e^{-i\omega t}}{\omega} + \mathbf{E}_1(\mathbf{r}, \omega + \omega_0) \frac{e^{-i(\omega + \omega_0)t}}{\omega + \omega_0} \right). \quad (21)$$

In (19) $\rho(\mathbf{r}, t)$ and $\mathbf{j}(\mathbf{r}, t)$ are the electron and current densities of the dipole which can be expressed through the polarization density $\mathbf{p}(\mathbf{r}, t)$:

$$\rho(\mathbf{r}, t) = -\nabla \cdot \mathbf{p}(\mathbf{r}, t) = -\frac{\partial}{\partial x_l} \left(p_{0l}(\mathbf{r}, \omega) e^{-i\omega t} + p_{1l}(\mathbf{r}, \omega) e^{-i(\omega + \omega_0)t} \right), \quad (22)$$

$$\mathbf{j}(\mathbf{r}, t) = \frac{\partial}{\partial t} \mathbf{p}(\mathbf{r}, t) = -i \left(\omega \mathbf{p}_0(\mathbf{r}, \omega) e^{-i\omega t} + (\omega + \omega_0) \mathbf{p}_1(\mathbf{r}, \omega) e^{-i(\omega + \omega_0)t} \right). \quad (23)$$

To linear order in vibrational coordinate $\mathbf{u}(t)$ and frequency ω_0 the total force acting on the point dipole can be written in the form

$$\mathbf{F}(t) = \mathbf{F}_{st}(\mathbf{r}_0) + \mathbf{F}_{dc}(t) + \mathbf{F}_{fric}(t). \quad (24)$$

Here the first term determines the conservative van der Waals force at the position $\mathbf{r} = \mathbf{r}_0$, and the second term is the change of the conservative van der Waals force during vibration, given by

$$\mathbf{F}_{dc}(t) = \mathbf{u}(t) \cdot \frac{d}{d\mathbf{r}_0} \mathbf{F}_{st}(\mathbf{r}_0) \quad (25)$$

The last term in (24) determines the friction force:

$$\mathbf{F}_{fric}(t) = i\omega_0\eta\mathbf{u}(t) = -\eta\dot{\mathbf{u}}(t) \quad (26)$$

Using results from Appendix C for motion parallel to the surface we obtain:

$$\begin{aligned} (\mathbf{F}_{fric})_x &= \frac{2\hbar V}{\pi} \int_0^\infty d\omega \left(-\frac{\partial n}{\partial \omega} \right) \\ &\times \left[\sum_{l=x,y,z} \left(\frac{\partial^2}{\partial x \partial x'} \text{Im} D_{ll}(\mathbf{r}, \mathbf{r}') \text{Im} \frac{\alpha(\omega)}{1 - \alpha(\omega) D_{ll}(\mathbf{r}_0, \mathbf{r}_0, \omega)} \right) \right. \\ &- 2 \quad | \alpha(\omega) |^2 \text{Re} \left(\frac{1}{(1 - \alpha^*(\omega) D_{zz}^*(\mathbf{r}_0, \mathbf{r}_0, \omega)) (1 - \alpha(\omega) D_{xx}(\mathbf{r}_0, \mathbf{r}_0, \omega))} \right) \\ &\left. \times \left(\frac{\partial}{\partial x} \text{Im} D_{xz}(\mathbf{r}, \mathbf{r}_0) \right)^2 \right]_{\substack{\mathbf{r}=\mathbf{r}_0 \\ \mathbf{r}'=\mathbf{r}_0}} \quad (27) \end{aligned}$$

and for the motion normal to the surface we obtain

$$\begin{aligned} (\mathbf{F}_{fric})_z &= \frac{2\hbar V}{\pi} \int_0^\infty d\omega \left(-\frac{\partial n}{\partial \omega} \right) \sum_{l=x,y,z} \left\{ \frac{\partial^2}{\partial z \partial z'} \left[\text{Im} D_{ll}(\mathbf{r}, \mathbf{r}', \omega) \right. \right. \\ &+ \text{Im} \left(\frac{\alpha(\omega) D_{ll}(\mathbf{r}, \mathbf{r}_0, \omega) D_{ll}(\mathbf{r}', \mathbf{r}_0, \omega)}{1 - \alpha(\omega) D_{ll}(\mathbf{r}_0, \mathbf{r}_0, \omega)} \right) \left. \right] \text{Im} \frac{\alpha(\omega)}{1 - \alpha(\omega) D_{ll}(\mathbf{r}_0, \mathbf{r}_0, \omega)} \\ &\left. + \left(\frac{\partial}{\partial z} \text{Im} \left(\frac{\alpha(\omega) D_{ll}(\mathbf{r}, \mathbf{r}_0, \omega)}{1 - \alpha(\omega) D_{ll}(\mathbf{r}_0, \mathbf{r}_0, \omega)} \right) \right)^2 \right\}_{\substack{\mathbf{r}=\mathbf{r}_0 \\ \mathbf{r}'=\mathbf{r}_0}} \quad (28) \end{aligned}$$

IV. Force of friction on physisorbed molecules

The friction force acting on the moving molecule usually is written in the form

$$\mathbf{F} = -M\eta\mathbf{V}, \quad (29)$$

where M is the mass and η is the coefficient of friction. For a physisorbed molecule we can neglect retardation effects. Formally this corresponds to limit $c \rightarrow \infty$ in the formulae for the Green's function. In Appendix B we show that in the non-retarded limit

$$D_{xx}(\mathbf{r}, \mathbf{r}') = \int \frac{d^2q}{2\pi} \frac{q_x^2}{q} R_p(\mathbf{q}, \omega) e^{i\mathbf{q}(\mathbf{x}-\mathbf{x}')-q(z+z')}, \quad (30)$$

$$D_{yy}(\mathbf{r}, \mathbf{r}') = \int \frac{d^2q}{2\pi} \frac{q_y^2}{q} R_p(\mathbf{q}, \omega) e^{i\mathbf{q}(\mathbf{x}-\mathbf{x}')-q(z+z')}, \quad (31)$$

$$D_{zz}(\mathbf{r}, \mathbf{r}') = \int \frac{d^2q}{2\pi} q R_p(\mathbf{q}, \omega) e^{i\mathbf{q}(\mathbf{x}-\mathbf{x}')-q(z+z')}, \quad (32)$$

$$D_{xz}(\mathbf{r}, \mathbf{r}') = i \int \frac{d^2q}{2\pi} q_x R_p(\mathbf{q}, \omega) e^{i\mathbf{q}(\mathbf{x}-\mathbf{x}')-q(z+z')}, \quad (33)$$

where R_p is the reflection factor for p -polarized electromagnetic waves. For physisorbed molecules we can neglect the imaginary part of the polarizability $\alpha(\omega)$. Then, to linear order in $\alpha(0)z_0^{-3}$, from (27,28) we get

$$\eta_{\parallel} = \frac{\hbar\alpha^2(0)}{2\pi M} \int_0^\infty d\omega \left(-\frac{\partial n}{\partial \omega} \right) \left[3 \frac{\partial^2}{\partial z^2} \text{Im} D_{zz}(z, z_0) \text{Im} D_{zz}(z_0, z_0) - \right. \\ \left. - 2 \left(\frac{\partial}{\partial z} \text{Im} D_{zz}(z, z_0) \right)^2 \right]_{z=z_0}, \quad (34)$$

$$\eta_{\perp} = \frac{3\hbar\alpha^2(0)}{\pi M} \int_0^\infty d\omega \left(-\frac{\partial n}{\partial \omega} \right) \left[\frac{\partial^2}{\partial z^2} \text{Im} D_{zz}(z, z_0) \text{Im} D_{zz}(z_0, z_0) + \right. \\ \left. \left(\frac{\partial}{\partial z} \text{Im} D_{zz}(z, z_0) \right)^2 \right]_{z=z_0}. \quad (35)$$

For $z_0 < \min(l, \hbar v_F/k_B T)$, where l is mean free path and v_F is the Fermi velocity, the reflection factor $R_p(\mathbf{q}, \omega)$ must be calculated using non-local optic. The non-local surface contribution to $\text{Im} R_p$ is given by³

$$(\text{Im} R_p)_{surf} = 2\xi \frac{\omega}{\omega_p} \frac{q}{k_F}, \quad (36)$$

where $\xi(q)$ depends on the electron density parameter r_s but typically $\xi(0) \approx 1$. Using this expression for $\text{Im} R_p$ in (34, 35) gives the surface contribution:

$$\eta_{\parallel surf} = 1.9 \frac{\xi^2 \hbar \alpha^2(0)}{M z_0^8} \left(\frac{k_B T}{\hbar \omega_p} \right)^2 \frac{1}{(k_F z_0)^2} \quad (37)$$

and $\eta_{\perp surf} = 8.4\eta_{\parallel surf}$. For physisorbed Xe on a metal one typically has $k_B T / \hbar \omega_p \sim 10^{-3}$. Using (37) we get $\eta_{\parallel} \sim 10^4 s^{-1}$ and $\eta_{\perp} \sim 10^5 s^{-1}$. These values are a factor $\sim 10^{-4}$ smaller than estimated in.²⁵ This means that in the case of physisorption on normal metals, the dissipative van der Waals interaction is determined by higher order processes that are not considered in the present theory. In the case of physisorption on high-resistivity material we can neglect non-local effects and use a local optic expression for reflection factor

$$R_p = \frac{\varepsilon(\omega) - 1}{\varepsilon(\omega) + 1} \quad (38)$$

In the case of constant conductivity σ the dielectric function has the form

$$\varepsilon = 1 + \frac{4\pi i \sigma}{\omega}. \quad (39)$$

As was shown in^{2,7} the maximum dissipation is achieved approximately at

$$4\pi\sigma \approx \frac{k_B T}{\hbar}. \quad (40)$$

At room temperature this corresponds to $\sigma \approx 10^2 (\Omega m)^{-1}$. Conductivities of this order are typical of semimetals such as carbon, or of a composite. In fact only a thin coating of the right conductivity would be required and this might arise from adsorbate layers derived from the gas phase.^{7,9} Using (34,35) and the expression for the Green's function

$$D_{zz}(z, z') = \frac{\varepsilon(\omega) - 1}{\varepsilon(\omega) + 1} \frac{2}{z + z'} \quad (41)$$

we get

$$\eta_{\parallel} = \frac{3\pi}{16} \frac{\hbar \alpha^2(0)}{M z_0^8} \left(\frac{k_B T}{4\pi \hbar \sigma} \right)^2 \quad (42)$$

and $\eta_{\perp} = 7\eta_{\parallel}$. In the case where the temperature is tuned to the conductivity so as to give maximum friction we get for Xe physisorption $\eta_{\parallel} \sim 10^9 s^{-1}$ and $\eta_{\perp} \sim 10^{10} s^{-1}$.

V. Force of friction on an STM tip

Another possible application of the dissipative van der Waals interaction is scanning probe spectroscopy. In the field of scanning probe spectroscopy

(STM, AFM) it is a common approximation to model the tip by a sphere with radius R . Consider distances $R \ll d \ll d_W \sim c\hbar/k_B T$ (at $T = 300\text{ K}$ we have $d_W \sim 10^5 \text{ \AA}$). In this case we can consider the sphere as a point dipole and in the formulae for the Green's function (Appendix B) we can put $p = iq$. Neglecting screening, from formulae (27, 28) we get

$$(\mathbf{F}_{fric})_x = \frac{\hbar V}{\pi} \int_0^\infty d\omega \left(-\frac{\partial n(\omega)}{\partial \omega} \right) \int_0^\infty dq q^4 e^{-2qd} \times \left\{ 2\text{Im}R_p(\omega)\text{Im}\alpha(\omega) + \left(\frac{\omega}{cq} \right)^2 \text{Im}R_s(\omega)\text{Im}\alpha(\omega) \right\} \quad (43)$$

and $(\mathbf{F}_{fric})_z = 2(\mathbf{F}_{fric})_x$. To simplify this expression we assume that $|\varepsilon(\omega)| \gg 1$ holds for all relevant frequencies. In the limit $d < |\varepsilon|^{-1/2} d_W$, where ε is taken at the characteristic frequency $\omega \sim k_B T/\hbar$, the p - and s -wave reflection factors become

$$R_p \approx \frac{\varepsilon - 1}{\varepsilon + 1}, \quad \text{Im}R_p \approx \frac{2\text{Im}\varepsilon}{|\varepsilon|^2}. \quad (44)$$

$$R_s = \frac{q - \sqrt{q^2 - (\omega/c)^2} \varepsilon}{q + \sqrt{q^2 - (\omega/c)^2} \varepsilon}, \quad \text{Im}R_s \approx \frac{1}{4} \left(\frac{\omega}{cq} \right)^2 \text{Im}\varepsilon \quad (45)$$

The polarizability of the sphere is determined by

$$\alpha = \frac{\varepsilon_t - 1}{\varepsilon_t + 2} R^3, \quad \text{Im}\alpha \approx \frac{3\text{Im}\varepsilon_t}{|\varepsilon_t|^2} R^3. \quad (46)$$

We describe the sphere using the same dielectric function (39) as the substrate:

$$\varepsilon_t = 1 + \frac{4\pi i \sigma_t}{\omega}.$$

In this limit we get the p -wave contribution

$$(\mathbf{F}_p)_x \approx 3 \frac{\hbar V}{d^5} \left(\frac{k_B T}{4\pi\hbar} \right)^2 \sigma^{-1} \sigma_t^{-1} R^3, \quad (47)$$

In the case of a good conductor at room temperature $k_B T/4\pi\hbar\sigma \sim 10^{-5}$, for a particle with $R = 10 \text{ \AA}$ and mass $M = 10^{-23} \text{ kg}$, moving $d = 10 \text{ \AA}$ above the surface, we get rather small coefficient of friction $\eta \sim 0.1 \text{ s}^{-1}$. However if

the conductivity is tuned to get the maximum friction, when $\sigma \approx \sigma_t$ and the condition (40) is fulfilled, we obtain $\eta \sim 10^7 s^{-1}$. For $|\varepsilon|^{-1/2} d_W < d < d_W$ we get the p -wave contribution

$$(\mathbf{F}_p)_x \approx 14\pi^{-5/2} \frac{\hbar V}{d^4} \left(\frac{k_B T}{\hbar} \right)^{5/2} \sigma^{-1/2} \sigma_t^{-1} c^{-1} R^3. \quad (48)$$

For $d < |\varepsilon|^{-1/2} d_W$ we get the s -wave contribution :

$$(\mathbf{F}_s)_x \approx \frac{\pi^3}{10} \frac{\hbar V}{d} R^3 \left(\frac{k_B T}{\hbar c} \right)^4 \frac{\sigma}{\sigma_t}, \quad (49)$$

and for $|\varepsilon|^{-1/2} d_W < d < d_W$ we get:

$$(\mathbf{F}_s)_x \approx 3.54\pi^{-3/2} \frac{\hbar V}{d^4} \left(\frac{k_B T}{\hbar} \right)^{5/2} \sigma^{-1/2} \sigma_t^{-1} c^{-1} R^3. \quad (50)$$

From (47) and (49) we conclude that $F_s > F_p$ for $0.2(cd_W/\sigma)^{1/2} < d < |\varepsilon|^{-1/2} d_W$. For a normal metal at room temperature $10^2 < d < 10^3 \text{ \AA}$. For $|\varepsilon|^{-1/2} d_W < d < d_W$, $F_s \approx F_p$. To estimate η for $R \gg d$ we can use an approximate approach. In⁹ it was shown that formula (43) can be obtained from an exact formula for frictional stress between two flat surfaces upon going to the limiting case of rarefied media. We can use the opposite approach to get the frictional stress between two flat surfaces from the friction force acting on point dipole. Neglecting screening effects, to a linear order in the velocity V , the frictional stress between two flat surfaces separated by a distance d , the p -wave contribution is determined by a formula^{4,9}

$$\sigma_{p\parallel} = \frac{\hbar V}{2\pi^2} \int_0^\infty d\omega \int_0^\infty dq q^3 e^{-2qd} \text{Im} R_{1p}(\omega) \text{Im} R_{2p}(\omega) \left(-\frac{\partial n(\omega)}{\partial \omega} \right), \quad (51)$$

The formula (51) can be obtained from formula (43) upon integration (43) over the volume of the semi- infinite body 2, and replacing

$$4\pi n\alpha \rightarrow 2R_{2p} = 2 \frac{\varepsilon_2 - 1}{\varepsilon_2 + 1} \quad (52)$$

where n is the density of the rarefied media. Using the same approach for the sphere with $R \gg d$ we get

$$\eta_{\parallel} = \frac{\pi}{6} \frac{\hbar}{M d^3} R \left(\frac{k_B T}{4\pi\hbar} \right)^2 \sigma^{-1} \sigma_t^{-1} \quad (53)$$

If the conductivity is tuned to the temperature then for a sphere with $R \sim 10^3 \text{ \AA}$, $d \sim 10 \text{ \AA}$ and $M \sim 10^{-17} kg$ we get $\eta \sim 10^3 s^{-1}$. The same formula (53) can be obtained if an STM tip is modeled by paraboloid, $z = (x^2 + y^2)/2R + d$, and integration is performed over the volume of paraboloid as it was described above, or over the surface of paraboloid using the formula

$$F_{p\parallel} = 2\pi \int_{-\infty}^{\infty} d\rho \rho \sigma_{p\parallel}(L(\rho)) \quad (54)$$

Here $L(\rho)$ denotes the tip-sample distance as a function of the distance ρ from the tip symmetry axis and a stress tensor $\sigma_{p\parallel}$ is taken from (51). This scheme was proposed in²⁸ for the calculation of the conservative van der Waals interaction. The error of this scheme is not larger than 5 – 10% in practice in an atomic force microscopy experiment, and 25% in a worst case situation.²⁹

If the conductivity is tuned to the temperature to give maximum dissipation then for the sphere with $R = 200 \text{ \AA}$, $d = 3 \text{ \AA}$ we get $\eta = F/V \sim 10^{-13} Ns/m$. This result is five order of magnitude smaller than what is observed experimentally for the friction force acting on the AFM-tip.^{12,13} Thus the dissipation of the translational energy of the AFM-tip can not be explained by Ohmic heating originating from a fluctuating electromagnetic field. This result is in an agreement with our earlier conclusion.⁸ One must consider other possible mechanism of the friction force acting on AFM-tip which can include phononic excitation or internal friction originating from the conservative van der Waals interaction.

VI. Local heating of a surface by an STM tip

It was pointed out by Pendry⁷ that the local heating of a surface by an STM tip can be used for local modification of a surface if the heat transfer is sufficiently great. To investigate the power of a hot tip to heat a surface Pendry modeled the tip as a hot sphere of the same radius R as the tip. This is a common approximation when calculating tunneling current and the same arguments justify its use for calculating heat tunneling. The heat flux between an STM tip and substrate can be calculated from the rate of work of the fluctuating electromagnetic field on the electrons of the tip which can be expressed by the formula

$$S = -\frac{dW}{dt} = -\int d^3r \langle \mathbf{j} \cdot \mathbf{E} \rangle \quad (55)$$

where integration is over the volume of the sphere. In the case $R \ll d$ we can consider the sphere as a point dipole and obtain

$$\begin{aligned} S &= i \int_{-\infty}^{\infty} d\omega \omega \langle p_{0l} (E_{0l}^*(\mathbf{r}_0) + E_l^{s*}(\mathbf{r}_0)) \rangle \\ &= i \int_{-\infty}^{\infty} d\omega \omega \sum_{l=x,y,z} \frac{\langle (p_l^f + \alpha(\omega) E_l^{s*}(\mathbf{r}_0)) (D_{ll}^*(\mathbf{r}_0, \mathbf{r}_0) p_l^{f*} + E_l^{s*}) \rangle}{|1 - \alpha(\omega) (D_{ll}(\mathbf{r}_0, \mathbf{r}_0))|^2} \\ &= 2\hbar \int_0^{\infty} d\omega \omega [n(\omega, T_t) - n(\omega, T)] \sum_{l=x,y,z} \frac{\text{Im}\alpha(\omega) \text{Im}(D_{ll}(\mathbf{r}_0, \mathbf{r}_0))}{|1 - \alpha(\omega) D_{ll}(\mathbf{r}_0, \mathbf{r}_0)|^2}, \end{aligned} \quad (56)$$

where T and T_t are the temperatures of the substrate and of the tip, respectively. Neglecting screening effects in formula (56) for distances $R \ll d \ll d_W$ we get⁹

$$\begin{aligned} S &= 2\frac{\hbar}{\pi} \int_0^{\infty} d\omega \omega (n(\omega, T_t) - n(\omega, T)) \int_0^{\infty} dq q^2 e^{-2qd} \\ &\quad \times \left\{ 2\text{Im}R_p(\omega) \text{Im}\alpha(\omega) + \left(\frac{\omega}{cq}\right)^2 \text{Im}R_s(\omega) \text{Im}\alpha(\omega) \right\} \end{aligned} \quad (57)$$

For small separations $d < l$ we can use (36) and (46) to get

$$S = \frac{3\pi^3 \xi R^3 k_B^4}{20k_F d^4 \hbar^3 \omega_p \sigma_t} (T_t^4 - T^4) \quad (58)$$

Assuming $T_t = 300 \text{ K}$, $d = 10 \text{ \AA}$, $R = 5 \text{ \AA}$, $\omega_p \sim 10^{16} \text{ s}^{-1}$, $\sigma_t \sim 10^{17} \text{ s}^{-1}$, and that the surface is cold so that there is no back flow of heat, we get $S \sim 10^{-15} \text{ W}$. The flow of heat will be confined to a very small area of diameter approximately the tip-surface separation d , and therefore the flux per unit area $S/d^2 \sim 10^3 \text{ W m}^{-2}$. This should be compared to the black body heat radiation^{9,22,23}:

$$\begin{aligned} S_{BB} &= \frac{\hbar}{8\pi^3} \int_0^{\infty} d\omega \omega n(\omega, T_t) \int_{q < \omega/c} d^2q (1 - |R_p(\omega)|^2) + [p \rightarrow s] \\ &\approx \frac{\hbar}{3\pi^2 c^2} \int_0^{\infty} d\omega \omega^3 \left(\frac{\omega}{4\pi\sigma}\right)^{1/2} n(\omega, T_t) \\ &= 0.4 \frac{k_B^4 T_t^4}{\hbar^3 c^2} \left(\frac{k_B T_t}{4\pi\hbar\sigma}\right)^{1/2} \end{aligned} \quad (59)$$

where $[p \rightarrow s]$ stands for the s -wave contribution obtained from the p -wave contribution by replacing R_p with R_s . For room temperature $S_{BB} \approx 0.5 \text{ Wm}^{-2}$. Thus there is large local enhancement of heating of the surface over that expected from the uniform black body radiation. As pointed out in⁷ a much larger effect is expected for high resistivity materials. In this case the heat flux between sphere and surface is given by^{7,9}

$$S_p \approx \frac{2\pi^2}{5} \left(\frac{R}{d}\right)^3 \left(\frac{k_B^4}{16\pi^2\hbar^3\sigma\sigma_t}\right) (T_t^4 - T^4). \quad (60)$$

The heat flux (60) is maximized when the condition (40) is fulfilled, which corresponds to conductivity $\sigma \approx 320(\Omega m)^{-1}$. In this case we get $S_p/d^2 \approx 5 \times 10^{10} \text{ Wm}^{-2}$. Let us now assume that the tip can be modeled by a paraboloid : $z = (x^2 + y^2)/2R + d$. To get a formula for the heat transfer between extended bodies we note that an exact formula for the heat transfer between two semi-infinite solids (without screening and retardation effects) is given by the formula:

$$S_z = \frac{\hbar}{\pi^2} \int_0^\infty d\omega \omega (n_1(\omega) - n_2(\omega)) \int_0^\infty dq q e^{-2qd} \text{Im} R_{1p}(\omega) \text{Im} R_{2p}(\omega) \quad (61)$$

This formula can be obtained from (57) upon integration over the volume of semi-infinite body with subsequent replacement (52). Applying this approach to a paraboloid tip, after integration over the volume of paraboloid and subsequent replacement of polarizability by the reflection factor R_{tp} of the tip we get

$$\begin{aligned} S_z &= \frac{\hbar R}{2\pi} \int_0^\infty d\omega \omega (n_t(\omega) - n(\omega)) \int_0^\infty dq e^{-2qd} \text{Im} R_p(\omega) \text{Im} R_{tp}(\omega) \\ &= \frac{\pi^3}{15} \left(\frac{R}{d}\right) \left(\frac{k_B^4}{16\pi^2\hbar^3\sigma\sigma_t}\right) (T_t^4 - T^4) \end{aligned} \quad (62)$$

For the same parameters as above, and for the conductivity which gives the maximum heat transfer (see above), we get $S_t \sim 10^{11} \text{ Wm}^{-2}$.

VII. Summary and conclusion

We have used a general theory of a fluctuating electromagnetic field to calculate the friction force acting on a small neutral particle moving near a

metal surface taking into account screening, non-local and retardation effects. A striking result of our study is that in the lowest order of the perturbation theory, the dissipation of energy for sliding physisorbed molecules is possible only due to the screening effects. The lowest order dissipative van der Waals interaction can be an important mechanism of vibrational energy relaxation for physisorbed molecules particularly for high-resistivity substrates. At room temperature this implies conductivities typical of semimetals such as carbon, or of metal-insulator composites. For physisorbed molecules on good conductor surfaces (e.g., Gold) the vibrational energy relaxation is dominated by higher order contributions (in the molecule-substrate coupling), as shown in Ref.²⁵ Another possible application of the present theory may be to atomic force microscopy experiments. At the optimized conditions, which at the room temperature corresponding to the conductivity $\approx 320 \Omega^{-1} m^{-1}$, the friction force acting on an AFM tip can be $F \approx \hbar V R / d^3$. In a typical case ($R = 300 \text{ \AA}$, $d = 3 \text{ \AA}$ and $V = 1 \text{ m/s}$) this gives $F \approx 0.1 \text{ pN}$. This result is five order of magnitude smaller than what was observed experimentally for the friction force acting on the AFM-tip.^{12,13} Other possible dissipation mechanisms include: phonon and electron excitation, and the internal friction. We have discussed several points of controversy with respect to some recent publications on fluctuation electromagnetic dissipative shear forces. We have shown that in the lowest order of the perturbation theory the linear (in sliding velocity) friction force, due to dissipative van der Waals interaction, vanish at zero temperature. Using the same approach we have calculated the heat transfer between an STM tip and metal surface. We have found that at the same optimized conditions as for the friction force, and at typical condition of AFM ($d = 10 \text{ \AA}$, $R = 10 \text{ \AA}$, $T = 300 \text{ K}$), the heat flux from the tip may be eleven order larger than the black body heat flux.

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Appendix A.

Dedkov *et. al.* have derived an expression for the friction force on a small neutral particle moving with the velocity V parallel to a flat surface,^{5,6} which is in sharp contrast to results of other authors.^{1,2,3,4,8,9,10} In particular, contrary to the known theoretical results, the authors of Ref.^{5,6} argue that the linear (in sliding velocity) friction force between bodies, due to a dissipative fluctuating electromagnetic field is non-vanishing at $T = 0$ K. The principal point of their theory^{5,6} is the expression for the energy dissipation rate of the fluctuating electromagnetic field in the system “particle- surface”:

$$-\frac{dW}{dt} = FV = \int \langle \mathbf{j}^{sp} \mathbf{E}^{ind} \rangle d^3r + \int \langle \mathbf{j}^{ind} \mathbf{E}^{sp} \rangle d^3r, \quad (A1)$$

where \mathbf{j}^{sp} , \mathbf{j}^{ind} are the spontaneous and induced component of the fluctuating current density in the particle; \mathbf{E}^{sp} is the electric field outside the metal in absence of the particle; \mathbf{E}^{ind} is the electric field from the metal induced by the spontaneous current density \mathbf{j}^{sp} . However (A1) is incorrect for the following reason. Formula (A1) determines the rate of the work performed by the external electric field in the laboratory reference frame in the volume of the particle. From energy conservation this rate of the work is equal with opposite sign to the rate of the work of the electric field in the volume of the metal. Since in the laboratory reference frame the metal is at rest the latter work will be converted to the heat in the metal volume. However the total dissipation of energy, which is determined by the rate of the work of the force of friction, includes also heat production in the volume of the particle, which is not included in formula (A1). The right relation between the rate of the work of the force of friction and the rate of the work of the external electric field in the volume of the particle can be obtained in the following way. The relation between the current densities in the laboratory reference frame and in the reference frame where the particle is at rest and the metal is moving with velocity $-\mathbf{V}$, in the non - relativistic limit, is given by: $\mathbf{j}^{sp(ind)} = \mathbf{j}^{sp(ind)'} + \rho^{sp(ind)} \mathbf{V}$, where $\mathbf{j}^{sp(ind)'}$ and $\rho^{sp(ind)}$ are the spontaneous (induced) current and charge density in the moving reference frame. Using this relation we get the relation between the rate of the work of the electric field in the volume of the particle in the laboratory and moving reference frame:

$$-\frac{dW}{dt} = \int \langle \mathbf{j}^{sp} \mathbf{E}^{ind} \rangle d^3r + \int \langle \mathbf{j}^{ind} \mathbf{E}^{sp} \rangle d^3r$$

$$\begin{aligned}
&= \int \langle \mathbf{j}^{sp'} \mathbf{E}^{ind} \rangle d^3r + \int \langle \mathbf{j}^{ind'} \mathbf{E}^{sp} \rangle d^3r \\
&\quad + \mathbf{V} \cdot \left(\int \langle \rho^{sp} \mathbf{E}^{ind} \rangle d^3r + \int \langle \rho^{ind} \mathbf{E}^{sp} \rangle d^3r \right) \\
&= -\frac{dW_0}{dt} + \mathbf{V} \cdot \mathbf{F}
\end{aligned} \tag{A2}$$

where $-dW_0/dt$ is the rate of the work in the moving reference frame, which is equal to the rate of the heat production in the volume of the particle, and \mathbf{F} the total force which acts on the particle which in the present case is equal to the friction force. We note that the electric field in the non-relativistic limit is the same in both reference frames. Thus, contrary to the point of view of Dedkov *et al.*, the rate of work is determined by Eq. (A2), instead of Eq. (A1). For a moving point dipole the spontaneous current density $\mathbf{j}^{sp}(\mathbf{r}, t)$ is given by

$$\mathbf{j}^{sp}(\mathbf{r}, t) = -i\delta(z - z_0)\mathbf{P}^f \int \frac{d^2q}{(2\pi)^2} (\omega + q_x V) e^{i\mathbf{q}\cdot\mathbf{r} - i(\omega + q_x V)t} \tag{A3}$$

and without screening effects, as assumed in,^{5,6} the induced electric field is given by

$$E_l^{ind}(\mathbf{r}, t) = \int \frac{d^2q}{(2\pi)^2} D_{lj}(\mathbf{q}, \omega + q_x V, z, z_0) p_j^f e^{i\mathbf{q}\cdot\mathbf{r} - i(\omega + q_x V)t} \tag{A4}$$

Using (A3, A4) we get

$$\begin{aligned}
\int \langle \mathbf{j}^{sp} \mathbf{E}^{ind*} \rangle d^3r &= -8 \int_0^\infty d\omega \int d^2q q e^{-2qz_0} A(\omega, T) \times \\
&\quad (\omega + q_x V) \text{Im} R_p(\omega + q_x V) \text{Im} \alpha(\omega)
\end{aligned} \tag{A5}$$

where we have used that in the non-retarded limit (see Appendix A):

$$\sum_{l=x,y,z} D_{ll}(\mathbf{q}, \omega, z, z_0) = 2D_{qq}(\mathbf{q}, \omega, z, z_0) = 4\pi q e^{-q(z+z_0)} R_p(\omega) \tag{A6}$$

After the Fourier decomposition of the fluctuating electric field from the metal

$$\mathbf{E}^s(\mathbf{r}, t) = \int \frac{d^2q}{(2\pi)^2} \mathbf{E}^s(\mathbf{q}, \omega, z) e^{i(\mathbf{q}\cdot\mathbf{r} - \omega t)}, \tag{A7}$$

the induced current density in the particle is given by

$$\begin{aligned} \mathbf{j}^{\text{ind}}(\mathbf{r}, t) = & -i\delta(z - z_0) \int \frac{d^2q}{(2\pi)^2} \int \frac{d^2q'}{(2\pi)^2} [\omega - V(q_x - q'_x)] \times \\ & \alpha(\omega - q_x V) \mathbf{E}^s(\mathbf{q}, \omega, z_0) e^{i\mathbf{q}' \cdot \mathbf{r} - i[\omega - V(q_x - q'_x)]t} \end{aligned} \quad (\text{A8})$$

From (A7,A8) the rate of work performed by the fluctuating electric field from the metal on the induced current in the particle, is given by

$$\int \langle \mathbf{j}^{\text{ind}} \mathbf{E}^{s*} \rangle d^3r = 8 \int_0^\infty d\omega \int d^2q q e^{-2qz_0} A(\omega, T) \omega \text{Im} R_p(\omega) \text{Im} \alpha(\omega - q_x V) \quad (\text{A9})$$

For the total rate of work performed by the electric field in the volume of the moving particle we get

$$\begin{aligned} -\frac{dW}{dt} = & 8 \int_0^\infty d\omega \int d^2q q e^{-2qz_0} A(\omega, T) \left[\omega \text{Im} R(\omega) \text{Im} \alpha(\omega - q_x V) - \right. \\ & \left. (\omega + q_x V) \text{Im} R_p(\omega + q_x V) \text{Im} \alpha(\omega) \right] \end{aligned} \quad (\text{A10})$$

Equation (A10) is very similar to one obtained in.^{5,6} However, the rate of work performed by the friction force is not determined by (A3) but is given by equation (A2). The rate of work performed by the electric field in the volume of the particle in the reference frame where the particle is at rest and the metal is moving with velocity $-V$ can be found in the similar way as in the laboratory system, and is given by

$$\begin{aligned} -\frac{dW_0}{dt} = & 8 \int_0^\infty d\omega \int d^2q q e^{-2qz_0} A(\omega, T) \\ & \times \left[(\omega - q_x V) \text{Im} R_p(\omega) \text{Im} \alpha(\omega - q_x V) - \omega \text{Im} R(\omega + q_x V) \text{Im} \alpha(\omega) \right] \end{aligned} \quad (\text{A11})$$

From (A2, A10, A11) we get the friction force

$$\begin{aligned} F = & 8 \int_0^\infty d\omega \int d^2q q q_x e^{-2qz_0} \\ & \times A(\omega, T) [\text{Im} R_p(\omega) \text{Im} \alpha(\omega - q_x V) - \text{Im} R_p(\omega + q_x V) \text{Im} \alpha(\omega)] \\ = & \frac{2\hbar}{\pi^2} \int_{-\infty}^\infty dq_y \int_0^\infty dq_x q_x q e^{-2qz_0} \left\{ \int_0^\infty d\omega [n(\omega + q_x V) - n(\omega)] \right. \\ & \times [\text{Im} R_p(\omega) \text{Im} \alpha(\omega + q_x V) + \text{Im} R_p(\omega + q_x V) \text{Im} \alpha(\omega)] \end{aligned}$$

$$\begin{aligned}
& + \int_0^{q_x V} d\omega \left(\frac{1}{2} + n(\omega) \right) \\
& \times [\text{Im} R_p(\omega) \text{Im} \alpha(\omega - q_x V) + \text{Im} R_p(\omega - q_x V) \text{Im} \alpha(\omega)] \Big\} \quad (\text{A12})
\end{aligned}$$

The formula is in complete agreement with the results in.^{1,2,4,9} To linear order in the sliding velocity V we get from (A12)

$$F = \frac{2\hbar V}{\pi} \int_0^\infty d\omega \frac{\partial n(\omega)}{\partial \omega} \int_0^\infty dq q^4 e^{-2qd} \text{Im} R_p(q, \omega) \text{Im} \alpha(\omega) \quad (\text{A13})$$

Appendix B.

Since equations (11-12) are translational invariant in the $\mathbf{x} = (x, y)$ plane, the Green's function $\tilde{D}_{ij}(\mathbf{r}, \mathbf{r}')$ can be represented by the Fourier integral:

$$\tilde{D}_{ij}(\mathbf{r}, \mathbf{r}') = \int \frac{d^2 q}{(2\pi)^2} e^{i\mathbf{q} \cdot (\mathbf{x} - \mathbf{x}')} \tilde{D}_{ij}(z, z', \mathbf{q}, \omega), \quad (\text{B1})$$

After the Fourier transformation it is convenient to choose the coordinate axes in the xy - plane along the vectors \mathbf{q} and $\mathbf{n} = \hat{z} \times \mathbf{q}$. Thus (11) and (12) become

$$\left(p^2 + \frac{\partial^2}{\partial z^2} \right) \tilde{D}_{nn}(z, z') = -\frac{4\pi\omega^2}{c^2} \delta(z - z') \quad (\text{B2})$$

$$\left(\left(\frac{\omega}{c} \right)^2 + \frac{\partial^2}{\partial z^2} \right) \tilde{D}_{qq}(z, z') - iq \frac{\partial}{\partial z} \tilde{D}_{zq}(z, z') = -\frac{4\pi\omega^2}{c^2} \delta(z - z') \quad (\text{B3})$$

$$p^2 \tilde{D}_{zq}(z, z') - iq \frac{\partial}{\partial z} \tilde{D}_{qq}(z, z') = 0 \quad (\text{B4})$$

$$p^2 \tilde{D}_{zz}(z, z') - iq \frac{\partial}{\partial z} \tilde{D}_{qz}(z, z') = -\frac{4\pi\omega^2}{c^2} \delta(z - z') \quad (\text{B5})$$

$$p^2 \tilde{D}_{qz}(z, z') + iq \frac{\partial}{\partial z'} \tilde{D}_{qq}(z, z') = 0 \quad (\text{B6})$$

$$p = \sqrt{\left(\frac{\omega}{c} \right)^2 - q^2} \quad (\text{B7})$$

Since the equations for \tilde{D}_{qn} and \tilde{D}_{zn} are homogeneous, these components of the Green function must vanish. Thus solving the system of equations (B2)

- (B6) is equivalent to solving altogether two equations: equation (B2) for \tilde{D}_{nn} , and the equation for \tilde{D}_{qq} which follows from equations (B3) and (B4):

$$\left(p^2 + \frac{\partial^2}{\partial z^2}\right) \tilde{D}_{qq}(z, z') = -4\pi p^2 \delta(z - z'). \quad (\text{B8})$$

\tilde{D}_{qz} , \tilde{D}_{zq} and \tilde{D}_{zz} for $z \neq z'$ can be obtained as

$$\tilde{D}_{qz} = -\frac{iq}{p^2} \frac{\partial}{\partial z'} \tilde{D}_{qq}; \quad \tilde{D}_{zq} = \frac{iq}{p^2} \frac{\partial}{\partial z'} \tilde{D}_{qq}; \quad \tilde{D}_{zz} = \frac{q^2}{p^4} \frac{\partial^2}{\partial z \partial z'} \tilde{D}_{qq} \quad (\text{B9})$$

In the vacuum region, $z > 0$, the solution of (B2) has the form

$$\tilde{D}_{nn}(z, z') = \frac{2\pi i \omega^2}{pc^2} e^{ip|z-z'|} + v_n e^{ipz} \quad (\text{B10})$$

At the boundary $z = 0$, the amplitude of the reflected wave is equal to the amplitude of the incident wave times the corresponding reflection factor. The Green's function \tilde{D}_{nn} is associated with the s -wave, and satisfies the boundary condition

$$v_n = R_s \frac{2\pi i \omega^2}{pc^2} e^{ipz'} \quad \text{for} \quad z = 0 \quad (\text{B11})$$

Thus

$$\tilde{D}_{nn}(z, z') = \frac{2\pi i \omega^2}{pc^2} \left\{ e^{ip|z-z'|} + R_s e^{ip(z+z')} \right\} \quad (\text{B12})$$

In (B12) the first and the second terms correspond to the Green's function D_{nn}^0 and D_{nn} , respectively. Equation (B8) for \tilde{D}_{qq} is similar to equation (B2) for \tilde{D}_{nn} , and taking into account that \tilde{D}_{qq} is associated with p - wave it can be obtained directly from (B12) by replacing $R_s \rightarrow -R_p$:

$$\tilde{D}_{qq} = \left(\frac{pc}{\omega}\right)^2 \tilde{D}_{nn} [R_s \rightarrow -R_p] \quad (\text{B13})$$

We note that in our approach the calculation of the reflection factors for s - and p - waves is considered as a separated problem, which, if necessary, can be solved by taking into account non-local effects. For the local optic case the reflection factors are determined by the well known Fresnel formulae:

$$R_p = \frac{\varepsilon p - s}{\varepsilon p + s}, \quad R_s = \frac{p - s}{p + s}, \quad (\text{B14})$$

where ε is the complex dielectric constant for metal and

$$s = \sqrt{\frac{\omega^2}{c^2}\varepsilon - q^2}. \quad (\text{B15})$$

The relations between Green's functions in the xyz and qnz coordinate systems are given by:

$$D_{xx} = \frac{q_x^2}{q^2}D_{qq} + \frac{q_y^2}{q^2}D_{nn}, \quad (\text{B16})$$

$$D_{xy} = D_{yx} = \frac{q_x q_y}{q^2}(D_{qq} - D_{nn}), \quad (\text{B17})$$

$$D_{xz} = \frac{q_x}{q}D_{qz}, \quad (\text{B18})$$

and so on.

Appendix C.

The forces from the electric and magnetic induction fields in (19), to linear order in the vibrational coordinate $\mathbf{u}(t)$, can be written in the form:

$$\begin{aligned} \int_{-\infty}^{\infty} d\omega \int d^3r \langle \rho \mathbf{E}^* \rangle &= \int_{-\infty}^{\infty} d\omega \int d^3r \left\langle p_l(\mathbf{r}, t) \frac{\partial}{\partial x_l} \mathbf{E}^*(\mathbf{r}, t) \right\rangle \\ &= \int_{-\infty}^{\infty} d\omega \frac{\partial}{\partial x_l} \left(\left\langle p_{0l} \left(1 + \mathbf{u}_0 \cdot \frac{\partial}{\partial \mathbf{r}} \right) (\mathbf{E}_0^*(\mathbf{r}, \omega) + \mathbf{E}^{s*}(\mathbf{r}, \omega)) \right\rangle \right. \\ &\quad \left. + [\langle p_{0l} \mathbf{E}_1^*(\mathbf{r}, \omega - \omega_0) \rangle + \langle p_{1l} (\mathbf{E}_0^*(\mathbf{r}, \omega) + \mathbf{E}^{s*}(\mathbf{r}, \omega)) \rangle] e^{-i\omega_0 t} \right)_{\mathbf{r}=\mathbf{r}_0}, \quad (\text{C1}) \end{aligned}$$

$$\begin{aligned} \frac{1}{c} \int_{-\infty}^{\infty} d\omega \int d^3r \langle \mathbf{j} \times \mathbf{B}^* \rangle &= \int_{-\infty}^{\infty} d\omega \left\{ \langle \mathbf{p}_0 \times \nabla \times (\mathbf{E}_0^*(\mathbf{r}) + \mathbf{E}^{s*}(\mathbf{r})) \rangle \right. \\ &\quad \left[\frac{\omega}{\omega - \omega_0} \left(\nabla \langle \mathbf{p}_0 \cdot \mathbf{E}_1^*(\mathbf{r}, \omega - \omega_0) \rangle - \frac{\partial}{\partial x_l} \langle p_{0l} \mathbf{E}_1^*(\mathbf{r}, \omega - \omega_0) \rangle \right) \right. \\ &\quad \left. + \frac{\omega + \omega_0}{\omega} \left(\nabla \left\langle \left(\mathbf{p}_1 + \mathbf{p}_0 \mathbf{u}_0 \cdot \frac{\partial}{\partial \mathbf{r}} \right) \cdot (\mathbf{E}_0^*(\mathbf{r}) + \mathbf{E}^{s*}(\mathbf{r})) \right\rangle \right) \right. \\ &\quad \left. \left. - \frac{\partial}{\partial x_l} \left\langle \left(p_{1l} + p_{0l} \mathbf{u}_0 \cdot \frac{\partial}{\partial \mathbf{r}} \right) (\mathbf{E}_0^*(\mathbf{r}) + \mathbf{E}^{s*}(\mathbf{r})) \right\rangle \right) \right] e^{-i\omega_0 t} \right\}_{\mathbf{r}=\mathbf{r}_0}. \quad (\text{C2}) \end{aligned}$$

From (C1-C2) it follows that the friction force is determined by the formula

$$\begin{aligned} \mathbf{F}_{fric} = & \frac{1}{2}\omega_0 \int_{-\infty}^{\infty} d\omega \left[\nabla \frac{\partial}{\partial \omega_0} \left(\frac{\omega}{\omega - \omega_0} \langle \mathbf{p}_0 \cdot \mathbf{E}_1^*(\mathbf{r}, \omega - \omega_0) \rangle \right. \right. \\ & \left. \left. + \frac{\omega + \omega_0}{\omega} \langle \mathbf{p}_1 \cdot (\mathbf{E}_0^*(\mathbf{r}) + \mathbf{E}^{s*}(\mathbf{r})) \rangle \right)_{\omega_0=0} - c.c. \right]_{\mathbf{r}=\mathbf{r}_0} \end{aligned} \quad (C3)$$

The calculation of (C3) is performed using the formulae

$$\begin{aligned} & \left(\frac{\partial}{\partial \omega_0} \frac{E_{1l}^*(\mathbf{r}, \omega - \omega_0)}{\omega - \omega_0} \right)_{\omega_0=0} \\ & = -\mathbf{u}_0 \cdot \frac{\partial}{\partial \mathbf{r}'} \left[\frac{\partial}{\partial \omega} \left(\frac{\alpha^*(\omega) D_{lk}^*(\mathbf{r}, \mathbf{r}_0, \omega)}{\omega (1 - \alpha^*(\omega) D_{kk}^*(\mathbf{r}_0, \mathbf{r}_0, \omega))} \right) \right. \\ & \quad \times (E_k^{s*}(\mathbf{r}', \omega) + D_{kk}^*(\mathbf{r}', \mathbf{r}', \omega) p_{0k}) + \frac{\alpha^*(\omega) D_{lk}^*(\mathbf{r}, \mathbf{r}_0, \omega)}{\omega (1 - \alpha^*(\omega) D_{kk}^*(\mathbf{r}_0, \mathbf{r}_0, \omega))} \\ & \quad \times \frac{\partial}{\partial \omega} \left(D_{ks}^*(\mathbf{r}_0, \mathbf{r}', \omega) \right) p_{0s}^* + \left. \frac{\partial}{\partial \omega} \left(\frac{D_{lk}^*(\mathbf{r}, \mathbf{r}', \omega)}{\omega} \right) p_{0k}^* \right]_{\mathbf{r}'=\mathbf{r}_0}, \quad (C4) \\ & \left(\frac{\partial}{\partial \omega_0} (\omega + \omega_0) p_{1l} \right)_{\omega_0=0} = \left(\frac{\partial}{\partial \omega_0} (\omega + \omega_0) \alpha(\omega + \omega_0) E_{1l} \right)_{\omega_0=0} \\ & = \mathbf{u}_0 \cdot \frac{\partial}{\partial \mathbf{r}'} \left[\frac{\partial}{\partial \omega} \left(\frac{\omega \alpha(\omega)}{1 - \alpha(\omega) D_{ll}(\mathbf{r}_0, \mathbf{r}_0, \omega)} \right) (E_l^s(\mathbf{r}', \omega) + D_{ll}(\mathbf{r}', \mathbf{r}', \omega) p_{0l}) + \right. \\ & \quad \left. \frac{\omega \alpha(\omega)}{1 - \alpha(\omega) D_{ll}(\mathbf{r}_0, \mathbf{r}_0, \omega)} \frac{\partial}{\partial \omega} \left(D_{lk}(\mathbf{r}_0, \mathbf{r}', \omega) \right) p_{0k} \right]_{\mathbf{r}'=\mathbf{r}_0}. \quad (C5) \end{aligned}$$

Using the following expression for the spectral density functions

$$\langle p_{0l} p_{0k} \rangle = 4\pi A(\omega, T) \delta_{lk} \text{Im} \frac{\alpha(\omega)}{1 - \alpha(\omega) D_{ll}(\mathbf{r}_0, \mathbf{r}_0, \omega)}, \quad (C6)$$

$$\langle p_{0l} E_k^{s*}(\mathbf{r}', \omega) \rangle = 4\pi A(\omega, T) \frac{\alpha(\omega)}{1 - \alpha(\omega) D_{ll}(\mathbf{r}_0, \mathbf{r}_0, \omega)} \text{Im} D_{lk}(\mathbf{r}_0, \mathbf{r}', \omega), \quad (C7)$$

$$\begin{aligned}
& \langle (E_l^s(\mathbf{r}', \omega) + D_{ll}(\mathbf{r}', \mathbf{r}', \omega)p_{0l}) (E_l^{s*}(\mathbf{r}, \omega) + D_{lk}^*(\mathbf{r}, \mathbf{r}_0, \omega)p_{0k}^*) \rangle \\
&= 4\pi A(\omega, T) \left[\text{Im} D_{ll}(\mathbf{r}, \mathbf{r}', \omega) + \frac{\alpha^*(\omega)}{1 - \alpha^*(\omega) D_{kk}^*(\mathbf{r}_0, \mathbf{r}_0, \omega)} D_{lk}^*(\mathbf{r}, \mathbf{r}_0, \omega) \right. \\
&\quad \left. \times \text{Im} D_{lk}(\mathbf{r}', \mathbf{r}_0, \omega) + D_{ll}(\mathbf{r}', \mathbf{r}', \omega) \text{Im} \left(\frac{\alpha(\omega) D_{ll}(\mathbf{r}, \mathbf{r}_0, \omega)}{1 - \alpha(\omega) D_{ll}(\mathbf{r}_0, \mathbf{r}_0, \omega)} \right) \right], \quad (\text{C8})
\end{aligned}$$

and (C4), (C5) for the vibration along the x - axis, (C3) is reduced to

$$\begin{aligned}
(\mathbf{F}_{fric})_x &= u_0 4\pi \omega_0 \int_{-\infty}^{\infty} d\omega A(\omega, T) \\
&\quad \times \frac{\partial}{\partial \omega} \left[\sum_{l=x,y,z} \left(\frac{\partial^2}{\partial x \partial x'} \text{Im} D_{ll}(\mathbf{r}, \mathbf{r}') \text{Im} \frac{\alpha(\omega)}{1 - \alpha(\omega) D_{ll}(\mathbf{r}_0, \mathbf{r}_0, \omega)} \right) \right. \\
-2 \quad &| \quad \alpha(\omega) |^2 \text{Re} \left(\frac{1}{(1 - \alpha(\omega)^* D_{zz}(\mathbf{r}_0, \mathbf{r}_0, \omega)^*) (1 - \alpha(\omega)^* D_{xx}(\mathbf{r}_0, \mathbf{r}_0, \omega))} \right) \\
&\quad \left. \times \left(\frac{\partial}{\partial x} \text{Im} D_{xz}(\mathbf{r}, \mathbf{r}_0) \right)^2 \right]_{\substack{\mathbf{r}=\mathbf{r}_0 \\ \mathbf{r}'=\mathbf{r}_0}}, \quad (\text{C9})
\end{aligned}$$

where we have used that for the vibrations parallel to the surface

$$\frac{\partial}{\partial x} D_{ll}(\mathbf{r}, \mathbf{r}) = 0, \quad (\text{C10})$$

$$\begin{aligned}
\frac{\partial}{\partial x} D_{lk}(\mathbf{r}, \mathbf{r}_0) \Big|_{\mathbf{r}=\mathbf{r}_0} &= - \frac{\partial}{\partial x} D_{lk}(\mathbf{r}_0, \mathbf{r}) \Big|_{\mathbf{r}=\mathbf{r}_0} = \\
&= \frac{\partial}{\partial x} D_{xz}(\mathbf{r}, \mathbf{r}_0) \Big|_{\mathbf{r}=\mathbf{r}_0} (\delta_{xl} \delta_{zk} - \delta_{xk} \delta_{zl}). \quad (\text{C11})
\end{aligned}$$

For vibration normal to the surface only the diagonal elements of the Green's function are non- vanishing and for this case (C3) reduce to

$$\begin{aligned}
(\mathbf{F}_{fric})_z &= u_0 4\pi A(\omega, T) \omega_0 \int_{-\infty}^{\infty} d\omega \frac{\partial}{\partial \omega} \sum_{l=x,y,z} \left\{ \frac{\partial^2}{\partial z \partial z'} \left[\text{Im} D_{ll}(\mathbf{r}, \mathbf{r}', \omega) \right. \right. \\
&\quad \left. \left. + \text{Im} \left(\frac{\alpha(\omega) D_{ll}(\mathbf{r}, \mathbf{r}_0, \omega) D_{ll}(\mathbf{r}', \mathbf{r}_0, \omega)}{1 - \alpha(\omega) D_{ll}(\mathbf{r}_0, \mathbf{r}_0, \omega)} \right) \right] \text{Im} \frac{\alpha(\omega)}{1 - \alpha(\omega) D_{ll}(\mathbf{r}_0, \mathbf{r}_0, \omega)} \right. \\
&\quad \left. \left. + \left(\frac{\partial}{\partial z} \text{Im} \left(\frac{\alpha(\omega) D_{ll}(\mathbf{r}, \mathbf{r}_0, \omega)}{1 - \alpha(\omega) D_{ll}(\mathbf{r}_0, \mathbf{r}_0, \omega)} \right) \right)^2 \right\}_{\substack{\mathbf{r}=\mathbf{r}_0 \\ \mathbf{r}'=\mathbf{r}_0}} \quad (\text{C12})
\end{aligned}$$

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